Influence of Li doping on morphology and luminescence of Ga_2O_3 microrods grown by a vapor-solid method

I. López, M. Alonso-Orts, E. Nogales, B. Méndez and J. Piqueras

Dpto. de Física de Materiales, Fac. Ciencias Físicas, Universidad Complutense de Madrid (Spain)

Abstract

Gallium oxide microrods have been grown by an evaporation-deposition method by using a precursor containing lithium in order to check the influence of such dopant on the morphology and physical properties of the obtained β-Ga_2O_3 structures. SEM studies show that the morphology is modified with respect to undoped gallium oxide, promoting the growth of micropyramids transversal to the microwire axis. Raman analysis reveals good crystal quality and an additional Raman peak centred at around 270 cm^{-1}, characteristic of these samples and not present in undoped monoclinic gallium oxide. The presence of the Li^+ ions also influences the luminescence emission by inducing a red-shift of the characteristic UV-blue defect band of gallium oxide. In addition, an intense sharp peak centred around 717 nm observed both by cathodoluminescence (CL) and photoluminescence (PL) is also attributed to the presence of these ions. The Li related luminescence features have been also investigated by PL excitation (PLE) spectra and by the temperature dependence of the luminescence.

Introduction

Gallium oxide has been the subject of extensive research during the last few decades due to its unique features, such as a wide band gap (around 4.8 eV), chemical stability and rather high electrical conductivity. In particular, applications such as luminescent devices [1], solar blind photodetectors [2, 3], substrate for GaN-family highly luminescent devices [4], as well as high power devices [5] have increased the interest on thin film or bulk β-Ga_2O_3 during the last years. On the other hand, micro- and nanostructures based on this oxide presents further points of interest and have been investigated for several purposes. Some examples are gas sensors [6] exploiting the high surface to volume ratio; multicolour light emitting transparent nanostructures due to its wide band gap suitable to host optically active ions [7-10]; and waveguiding applications [11] or resonant cavities [12]. The effective doping of small dimensional structures is necessary in order to tune their physical and chemical properties and widen the applications field. However, it usually becomes a challenge and several techniques, such as in-situ doping during growth, or post growth doping by ion implantation or diffusion, have been proposed [13]. We have successfully doped Ga_2O_3 nanowires with several impurities, including transition metal and rare earth ions, so far by these techniques [7-9].

Lithium is of potential interest as gallium oxide dopant in order to modify its ionic conductivity for electrical energy storage applications [14]. So far, ionic conductivity of β-Ga_2O_3has been discussed and it was attributed to either to Ga^{3+} vacancies [15] or to O^{2-} vacancies [16]. Besides, it is interesting to study how the addition of Li into the precursors during the thermal growth process could influence the morphology and luminescence properties of the Li doped Ga_2O_3 microstructures. In this work, in-situ doping with Li has been carried out during the growth of the microstructures and their morphological, structural and luminescence features have been investigated.

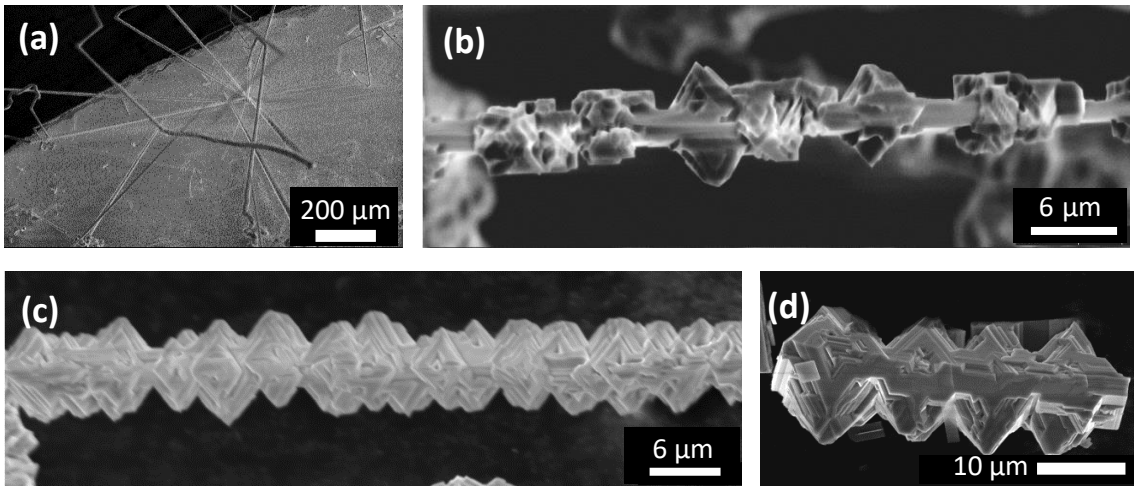
Experimental

The microstructures have been grown by a vapour-solid mechanism in a furnace, as reported elsewhere [8]. The precursors were in this case: metallic gallium and Li_2CO_3 powders. They were placed onto a Ga_2O_3 (60% wt.) + Li_2CO_3 (40% wt.) pellet, which behaved as substrate. The pellet was heated in a tube furnace at 950 ºC for 7 hours under an inert gas flow, resulting on the growth of microrods as described below. A reference sample was grown in the same conditions but with no Li_2CO_3 powders.

SEM analysis was performed in a Leica Stereoscan 440 scanning electron microscope (SEM). Cathodoluminescence (CL) analysis was also carried out in this microscope. Raman and photoluminescence (PL) local spectra were obtained with a Horiba Jobin Yvon LabRAM HR800 confocal microscope, where excitation was obtained with the 325 nm line of a HeCd laser. X-ray photoelectron spectroscopy (XPS) studies have been performed in the Spectromicroscopy line in Elettra synchrotron, in Trieste, Italy. PL excitation (PLE) spectra were acquired in a Jobin Yvon spectrofluorimeter equipped with a xenon lamp.

Results and discussion

Figure 1 shows SEM images of several Li doped microrods. Figure 1(a) presents a low magnification image with several long structures grown on the pellet substrate. Figures 1(b)-(d) show the characteristic morphological features found in Li doped samples, i.e. transversal pyramids that grow on the lateral sides of the main rods. It has been previously reported that during vapour-solid (VS) growth the presence of different doping elements in the precursors can result in notable morphological changes, such as the formation of branches [9], crossing wires [17] and complex hierarchical structures [18]. However, these morphological pyramidal features have not been observed with other dopants or in undoped gallium oxide microstructures grown under similar conditions, as shown in figure 1(e). This fact supports that the presence of Li during the growth could be the responsible for such morphological features.



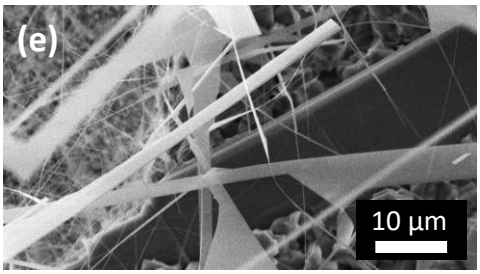


Figure 1. SEM images of Li doped Ga_2O_3microwires. (a) General view of the microwires grown on the substrate surface (b) – (d) details of several structures with lateral pyramids. (e) Representative image from a sample grown in the same conditions, but with no presence of Li_2CO_3.

In order to study the crystalline quality of these microrods, micro-Raman analysis has been performed in the confocal microscope. A representative Raman spectrum is shown in figure 2. The typical peaks related to monoclinic β-Ga_2O_3 – 144, 169, 200, 320, 345, 416, 475, 630, 652, 657 and 766 cm^{-1} – are detected (see ref. [9] and inset in figure 2). However, an additional peak centred at 270 cm^{-1}, not present in undopedGa_2O_3, is also observed. The inclusion of lighter atoms in the host could result in the appearance of new peaks in the Raman spectrum at high frequencies [9, 19], which could explain the presence of this additional peak. Besides, a higher intensity of the 652 cm^{-1} peak with respect to the one at 658 cm^{-1} is observed. In previous reports, it was an indication of the presence of dopants [9].

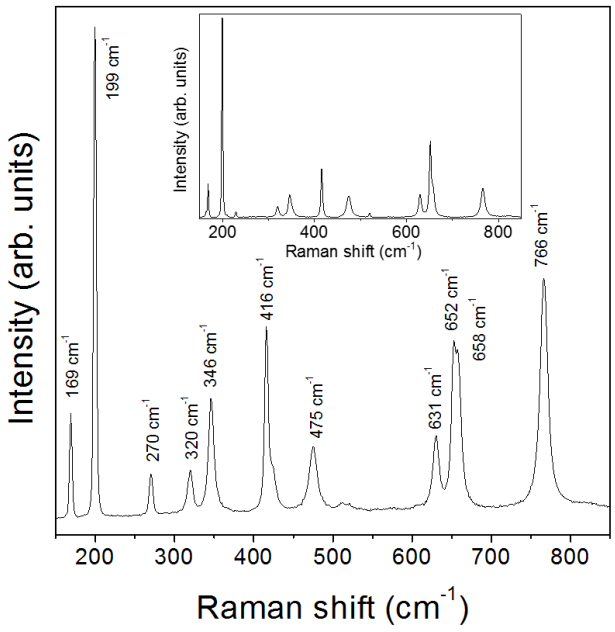


Figure 2. Local, micro-Raman spectrum from a Li doped β-Ga_2O_3 microstructure. Inset: Raman spectrum of the reference undoped sample.

Due to the low atomic number of Li, it is not possible to detect this element by energy dispersive X-ray spectroscopy (EDS) in SEM. Alternatively, in order to get evidence of the presence Li ions in the microstructures we have carried out micro-XPS measurements. Figure 3 shows a representative XPS spectrum acquired with a photon energy of 74 eV. Ga 3d line at 20 eV is observed, as well as the Ga_2O_3 valence band. Li 1s line should appear at around 55 eV. The fact that it cannot be detected by XPS indicates that, near the surface, it is present in a very low quantity, typically below around 1 atom %. The valence band edge is deduced to be at around 3

eV below Fermi level from this spectrum. This value is similar to that obtained in Sn doped Ga_2O_3 [20] and expected for this type of oxide.

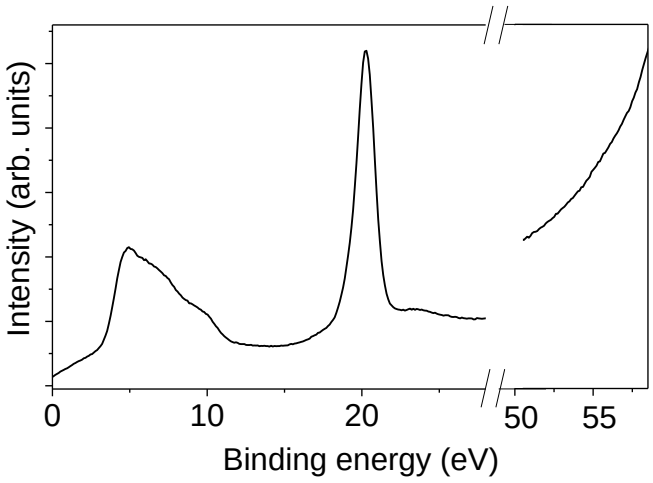


Figure 3. Local XPS spectrum from one of the Li doped microstructures acquired with a beam energy of 74 eV.

The influence of Li on the luminescence properties of Ga_2O_3 is also of high interest as this oxide presents strong luminescence in different regions of the UV-vis-IR range, which can be used for different photonic applications [7-9, 11-12]. Figure 4(a) shows the CL room temperature emission from the Li doped microrods (solid line), along with the spectrum in the same conditions of the undoped reference sample (dashed line). The CL spectrum of the Li doped sample shows in the UV-blue region the intense, well known defect-related band of gallium oxide [21] red shifted with respect to the undoped one. Several features appear in the 400 nm region of the Li doped sample, which might be associated to some absorptions of the species responsible with the red, sharp bands. Besides, a sharp and intense near IR luminescence peak is observed, centred at 717 nm. Red-infrared emission bands and sharp peaks have been previously reported for N [22], Cr [7, 11, 12] or Eu [8, 23] doped gallium oxide at room temperature. However, none of these emissions resembles this very well defined sharp peak shown in figure 3. Figure 4(b) shows a detail of this non-expected emission. It can be seen that a broad band formed by several peaks is superimposed to the narrow dominant 717 nm peak with a FWHM of about 50 nm. This band reminds of phonon-assisted transitions with low Huang-Rhys factor, similar to that observed in Cr^{3+} doped Ga_2O_3 at room temperature [7].

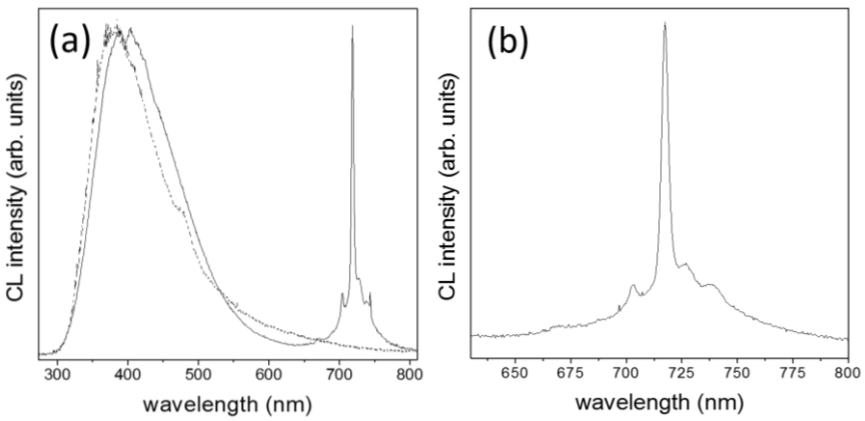


Figure 4. (a) Room temperature CL emission from Ga_2O_3:Li microstructures (solid line) and reference undoped sample (dashed line). (b) detail of the red luminescence band observed in Ga_2O_3:Li microstructures

In order to further analyse the 717 nm emission, temperature dependence measurements were carried out, and the results are displayed in figure 5. Figure 5a shows the temperature evolution of the luminescence when normalizing to the UV band in the interval 100 – 300 K. The overall intensities of both bands decrease when temperature raises (not shown), but the quenching rate for the broad UV-blue band is higher than that for the sharp, infrared emission, as seen in fig. 5(a). The relative intensity of the infrared peak clearly increases with respect to that of UV band when temperature is raised. On the other hand, the UV-blue band is redshifted from about 366 nm to some 400 nm and broadened when temperature increases. A similar behaviour of this band was observed for Sn, Cr, codoped gallium oxide nanostructures [9]. The sharp infrared peak keeps a similar width and shows only a slight redshift of about 2 nm.

Figure 5(b) shows a detail of the red peak at T = 300 K and 100 K. It is observed that the broad band below the main peak is stronger at 300 K, indicating that it is thermally activated, as compared to the sharp peak at 717 nm. Two peaks at around 730 nm and 740 nm are still present in the spectrum at 100 K.

The 717 nm infrared emission has not been previously observed in Ga_2O_3doped with other elements. In a previous report [24] long-lived luminescence band centred at 724 nm was observed in Li doped TiO_2 and it was assigned to the presence of Li^+ ions. It is well known that the optical emission properties of the ions can differ from one host to another [25], which could explain the differences in the position and the width of the peak from TiO_2 to Ga_2O_3 host. Li^+ presents several intraionic allowed transitions, among which the ^2S - $^2P_0$ transition has been reported to be at 713.5 nm [26]. Therefore, we tentatively assess the origin of the 717 nm infrared peak to be due to Li ions within the Ga_2O_3 host. Furthermore, it could be due to intraionic transitions of Li^+, although other radiative processes related to the presence of Li^+ cannot be ruled out.

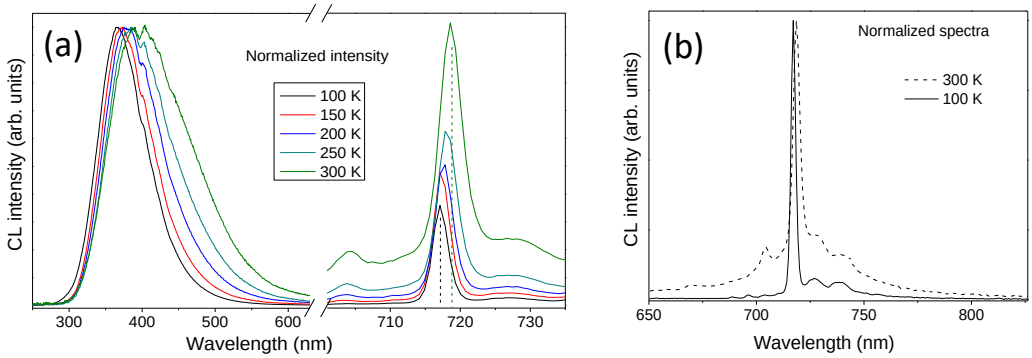


Figure 5. (a) Temperature evolution of the intensity of the Ga_2O_3:Li microwires luminescence normalized to the UV emission intensity. (b) Infrared peak at 300 K and 100 K. At low temperature, the broad band is almost quenched.

In order to elucidate the excitation mechanisms of the infrared luminescence peak in the Ga_2O_3 microwires, PLE spectra were acquired by selecting λ_{emi} = 717 nm, as shown in figure 6. The peak at 255 nm (around 4.9 eV) corresponds well with the interband transition for Ga_2O_3. Therefore, excitation via energy transfer by the interband electron-hole pairs occurs for this transition. A

similar result was observed in Ga_2O_3:Cr for the excitation of the Cr^{3+} emission at 690 nm [7]. However, in this case, strong excitation is also obtained in the 300 - 375nm range, which is marked with an arrow in the PLE spectrum shown in Figure 6(a). This fact is tentatively related to the presence of defects within the band gap, which effectively excite this red luminescence. This broad excitation band was not observed, for example, in the Ga_2O_3:Cr samples [7].

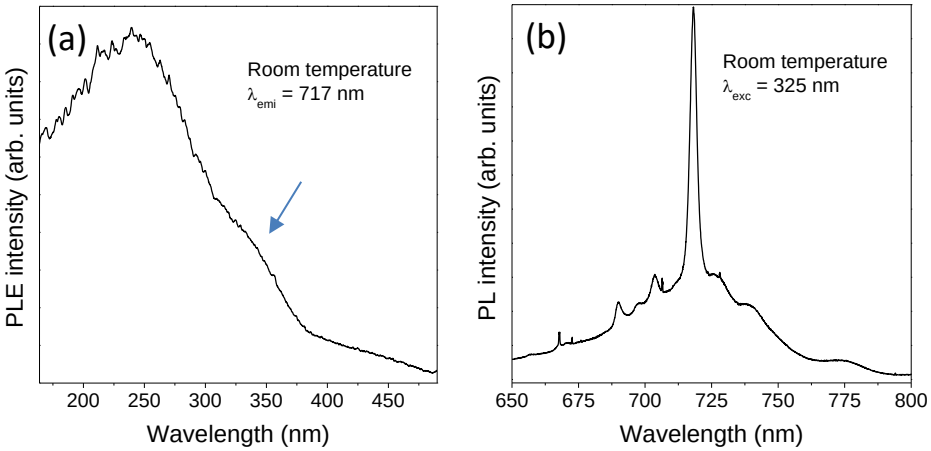


Figure 6. (a) PLE spectrum of the 717 nm peak at room temperature. (b) PL spectrum with excitation wavelength at 325 nm at room temperature.

Conclusions

Li doped Ga_2O_3 microrodshave been grown by a vapour-solid mechanism in a single thermal treatment. The morphology of the microrods is modified, with respect to structures grown in absence of dopant, by the presence of lithium during the growth, yielding the formation of triangular lateral protuberances on the sides of elongated microwires. Raman spectra show the appearance of a peak at 270 cm^{-1} that is not observed in other Ga_2O_3 samples, and is assigned to the presence of Li ions within the monoclinic gallium oxide host. An intense, sharp luminescence peak in the near-IR region has been detected around 717 nm by CL and PL analysis. Its origin is tentatively related to the presence of Li^+ ions. It is excited via Ga_2O_3interband excitation and by defect band excitation.

Acknowledgements

The authors are grateful to Dr. Alexey Varinov at the Elettra Sincrotrone Trieste for useful advises on XPS measurements. This work has been supported by MINECO/FEDER through Project MAT 2015-65274R, by MINECO through projects MAT 2012-31959 and Consolider CSD 2009-00013 and by EEA Grants NILS project 008-ABEL-CM-2013.

References

[1] Wellenius P, Suresh A and Muth J F 2008 *Appl. Phys. Lett.* **92** 021111
[2] Chen X, Liu K, Zhang Z, Wang C, Li B, Zhao H, Zhao D and Shen D 2016 *ACS Appl. Mater. Interfaces* **8** 4185
[3] López I, Castaldini A, Cavallini A, Nogales E, Mendez B and Piqueras J 2014 *J. Phys. D: Appl. Phys.* **47** 415101
[4] Víllora E G, Shimamura K, Kitamura K, Aoki K and Ujiie T 2007 *Appl. Phys. Lett.* **90** 234102

[5] Sasaki K, Kuramata A, Masui T, Víllora E G, Shimamura K and Yamakoshi S 2012 *Appl. Phys. Express* **5** 035502
[6] Mazeina L, Perkins F K, Bermudez V M, Arnold S P and Prokes S M 2010 *Langmuir* **26** 13722
[7] Nogales E, Garcia J A, Mendez B and Piqueras J 2007 *J. Appl. Phys.* **101** 033517
[8] E. Nogales, Mendez B, Piqueras J and Garcia J A 2009 *Nanotechnology* **20** 115201
[9] Lopez I, Nogales E, Mendez B, Piqueras J, Peche A, Ramírez-Castellanos J and González-Calbet J M 2013 *J. Phys. Chem. C* **117** 3036
[10] Wang X-S, Li W-S, Situ J-Q, Ying X-Y, Chen H, Jin Y and Du Y-Z 2015 *RSC Adv.* **5** 12886
[11] E. Nogales E, Garcia J A, Mendez B and Piqueras J 2007 *Appl. Phys. Lett.* **91** 133108
[12 Lopez I, Nogales E, Mendez B and Piqueras J 2012 *Appl. Phys. Lett.* **100** 261910
[13] Ronning C, Borschel C, Geburt S, Niepelt R 2010 *Mater. Sci. Eng. R* **70** 30
[14] Goodenough J B and Manthiram A 2014 *MRS Communications* **4** 135
[15] Harwig T, Kellendonk F 1978 *J. Solid State Chem.* **24** 255
[16] Blanco M A, Sahariah M B, Jiang H, Costales A and Pandey R 2005 *Phys. Rev. B* **72**, 184103
[17] Martínez-Criado G, Segura-Ruiz J, Chu M-H, Tucoulou R, Lopez I, Nogales E, Mendez B and Piqueras J 2014 *Nano Lett.* **14** 5479
[18] Lopez I, Nogales E, Mendez B, Piqueras J, Castaldini A and Cavallini A 2014 *Mat. Res. Express* **1** 025017
[19] *Raman Scattering in Materials Science* 2010 Weber W H, Merlin R, Springer, New York
[20] Lopez I, Nogales E, Hidalgo P, Mendez B and Piqueras J 2010 *phys. stat. sol. a* **209** 113
[21] Binet L and Gourier D 1998 *J. Phys. Chem. Solids* **59** 1241
[22] Song Y P, Zhang H Z, Lin C, Zhu Y W, Li G H, Yang F H, and Yu D P 2004 *Phys. Rev. B* **69** 075304
[23] Wellenius P, Suresh A and Muth J F 2008 *Appl. Phys. Lett.* **92** 021111
[24] Kallel W, Bouattour S, Vieira Ferreira L F, Botelho Rego A M 2009 *Mater. Chem. Phys.* **114** 304
[25] *Optical spectroscopy of inorganic solids* 1989 Henderson B and Imbusch G F, Clarendon Press, Oxford
[26] Wiese W L and Fuhr J R 2009 *J. Phys. Chem. Ref. Data* **38** 565